THERMAL DEGRADATION OF SHALE OIL

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ABSTRACT

A new procedure has been developed to study the mechanisms of shale oil
degradation, which occurs during the VMIS retorting process. The very com-
plex processes of oil degradation have been studied under carefully controlled
conditions of temperature, residence time, carrier gas flow rate, etc. The
experiments presented in this study have been designed to separate the three
potential oil loss mechanisms, namely, (1) low temperature coking (liquid
phase), (2) successive distillation (liquid phase), and (3) high temperature
cracking (vapor phase). The shale oil from Occidental's retort No. 6 has
been used as a starting material. The steady state nature of operation used
here makes it possible to achieve an accurate material balance for degraded
products. In the liquid phase oil degradation experiments, oil was heated
to 450°C at a linear heating rate of 1°C/min in both an autogenous atmosphere
and using various sweep gases such as steam, N_2, CO_2, CO and H_2. Low tempera-
ture coking showed only minor losses. A 35 percent oil loss occurred during
successive distillation under autogenous conditions. It was reduced to 15
percent by injection of sweep gases, especially steam. A tubular continuous
flow reactor was used to study the vapor phase degradation under steady state
conditions of temperatures (425 to 625°C) and residence time (2 to 10 sec)
with nitrogen and steam as carrier gases. A 3^2 factorial design was conducted
to assess the influence of temperature and residence time on oil degradation.
The kinetic data were analyzed by a first order rate equation giving an acti-
vation energy of 17.3 kcal/mole.

INTRODUCTION

Shale oil is a potentially important fossil fuel which could augment energy
supplies in future years. Modified in-situ retorting of oil shale may offer
a new and viable method for extracting oil from shale. A key consideration in
this new and rapidly developing technology is the problem of maximizing oil
recovery from each underground retort, since thousands of retorts will be
required. In this process gas composition, temperature, heating rate, particle
size distribution and retorting rates are major factors. Low oil yields have
been observed from tests on large retorts. Since the oil losses that occur
during the pyrolysis of oil shale are quite substantial, a considerable amount
of work is directed towards the elucidation of oil loss mechanisms. [1-12] Within
a retort, one encounters a situation downstream of the retorting front where
product oil condenses on the raw shale. Oil trapped in this zone can be exposed
to modest temperatures for months. This leads to low temperature oil degrada-
tion by coking. At the leading edge of the thermal wave, a continuous vapori-
zation and condensation of oil will occur which may also cause significant oil
degradation. In the VMIS process, loss in oil yields also results from the

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large particles and wide size distributions. The large blocks are heated at a slower rate than the surrounding matrix because of poor heat transfer. The exposure of oil vapor, liberated from large particles, to high temperatures leads to its thermal degradation. Several factors contribute to the degradation mechanisms among which residence time, temperature, and sweep gas atmosphere are prominent candidates. It is well known that oil shales (raw and spent) could catalytically initiate certain undesired reactions leading to oil loss. It is also conceivable that the mechanism responsible for liquid phase oil degradation is different from that for vapor phase one.

When hydrocarbons are brought to high temperature, they undergo thermal cracking via free radical mechanisms. The radicals thus formed can undergo scission to give large amounts of ethylene. Jacobson, et al[1] observed that during oil shale pyrolysis, ethylene/ethane ratio increased with temperature. Based on these findings, they developed the retorting index (R. I.) which is given by the following equation:

$$R.I. = T° (F) = \frac{1000}{0.8868 - 0.4007 \log \frac{\text{ethylene}}{\text{ethane}}}$$

The ratio of ethylene to ethane was found to depend upon the heating rate and residence time. Campbell, et al[2], have studied the effect of heating rate and particle size on oil evolution and intraparticle oil degradation. They correlated the alkene/alkane ratio to the liquid phase oil degradation (coking).[3] Duringthe last few years, the alkene/alkane ration has been used extensively as an index of thermal degradation.[5-9] Burnham, et al [10,15,16] have studied the oil degradation mechanism in vapor phase with raw oil shale as the starting material. It was found that the alkene to alkane ratio decreases with increased coking while it increases with increase in cracking of the shale oil. If both reactions occur simultaneously one cannot use this ratio as an index of oil degradation. Hence, a naphthalene/$(C_{11} + C_{12})$straight chain hydrocarbons ratio was recommended by Burnham, et al[15] as an index of cracking or vapor phase oil loss.

The experiments presented in this study were designed in such a way as to separate the following processes:

      1.   Low temperature coking (liquid phase).
      2.   Successive distillation (liquid phase), and
      3.   High temperature cracking (vapor phase).

Such a design yielded information about the most important features of liquid and vapor phase oil degradation. In this study, shale oil was used to permit accurate characterization of the starting material in contrast to other studies which used the oil generated by heating oil shale in a small laboratory-scale retort. Advantages and disadvantages of the approach used in the present study are described below. Advantages are as follows:

      1.   The feed can be well characterized and compared to the degraded product.
      2.   Since the experiment is operated in a steady state manner, an accurate material balance for degraded products is achieved.

3. Because of the steady state and continuous nature of operation used here, residence time can be determined and controlled more precisely as compared to batch operation studies. In the latter studies the batch method of oil generation makes the determination and control of residence time rather difficult, and introduces time varying feed rate.

4. It is possible to investigate the effect of mineral matter present in the shale oil either as colloidal suspension or in solution. By using the total molecular weight distribution, effects such as auto-catalytic cracking, if it occurs, can be studied.

5. The shale oil used in this study was from Occidental's retort No. 6 and was thus characteristic of the oil product from a large-scale retort.

The shortcomings of this approach are few and may be overcome.

1. The feed oil has already been exposed to some undetermined amount of degradation which may affect its subsequent behavior. One way to overcome this problem is to test the oil from various sources.

2. Storage of the oil for a prolonged time may alter its properties and composition. Very little literature data are available on the effect of storage. This problem can be avoided by obtaining fresh samples of oil.

3. Oil may contain a colloidal suspension of minerals which might catalyze the oil degradation or cracking. This phenomenon needs further study involving filtration or demineralization of oil.

In this paper, results obtained by subjecting the oil to coking conditions (low temperature soaking and successive distillation) will be compared to those obtained by treating the shale oil under cracking conditions. In addition, effect of carrier gas such as steam, N_2, CO_2, CO and H_2 on low temperature liquid phase degradation will be discussed.

<center>EXPERIMENTAL PROCEDURE</center>

LIQUID PHASE DEGRADATION

Apparatus

A standard bench-scale glassware assembly was used. The apparatus consisted of a heating mantle, a 4-necked flask (3000 ml), stirrer, sparger, condensers and receivers for liquid, and gas samples. In low-temperature soaking experiments, a reflux condenser was used to return the oil vapor to the heating flask, while in the successive distillations a regular condenser was used and low boiling fractions were collected in the receivers. When experiments were performed in an autogenous environment, a stirrer was used to ensure uniform mixing and avoid spurting. When the experiments were carried out in sweep gas environment a sparger was used to bubble the gas through the shale oil.

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Procedure

Low-Temperature Soaking

About 1 liter of shale oil was placed in the 4-necked flask. The flask was covered with glass wool in order to insulate it from the surroundings. The flask was then heated gradually at the rate of 1°C/min to the desired temperatures (170 to 400°C) with constant stirring. The temperature was controlled within ±1°C by means of a temperature controller and a variac. Time of thermal treatment was about 10 to 12 hours. The low-boiling, condensable oil fractions were collected in the receiver while the gas produced, if any, was collected in the gas samplers. The shale oil (before and after thermal treatment) and condensate were analyzed on a capillary column gas chromatograph as described earlier,[13] while the hydrocarbon and permanent gases were analyzed by using 1/8 in. i.d. 6-ft long Poropak Q and Molecular Sieve 13X columns.

Successive Distillation

The procedure was similar to that described in the preceding paragraph except that after each distillation the condensate was mixed with the residue in the still and the mixture was redistilled until no appreciable loss due to coke formation or gas evolution was observed. The carrier gas was introduced through the side tube during the distillation.

The liquid products (condensate and residue in the flask) were analyzed on a SP-2100 fused silica column by using an HP 5840 A gas chromatograph; the gas analysis was performed on Poropak Q and carbosieve columns by using an HP 5840 gas chromatograph. Condensate and residue in the distillation flask were weighed. A known amount of methylene chloride was then added to the distillation flask so as to dissolve the tar-like organic matter. The flask was reweighed, the difference between the two readings was taken as the amount of coke formed during these experiments. By measuring the amount of gas, condensate and residue, a material balance of 98 percent was achieved.

VAPOR PHASE OIL DEGRADATION

Apparatus

A tubular continuous flow reactor, with on-line gas chromatograph, was used to study the vapor phase oil degradation under steady state conditions of temperature and residence time. Fisher and Porter flow meters (model 10A1379) were used to control the flow rates of nitrogen and water before they entered the perheaters. Shale oil was injected into the stream of carrier gas at a steady rate by means of a Sage syringe pump model 341. Glass-lined stainless-steel tubes (8 mm i.d., 200 mm long) were used to generate steam from water and to heat the fluid mixture to about 400°C before its entry into the reactor. The maximum residence time of the fluid in the preheaters was less than 1 sec (at the lowest flow rate). The thermal degradation of oil (at 400°C) at the exit of the preheaters was predetermined; it was less than 1 percent. An empty quartz tube (25 mm i.d. and 300 mm long) served as a reactor in the present study. The reactor was heated by means of a Lindberg heavy duty tubular furnace, the temperature of which was controlled within ±1°C by a Lindberg temperature controller. The product collection assembly consisted of condensers and receivers, and either a filter or an electrostatic precipitator to

prevent the oil vapor (aerosol) from escaping with the uncondensable gases. The gases passed through a flow meter and a gas sampling valve to the gas chromatograph (HP 5840) for periodic analysis.

Procedure

The reactor and preheaters were heated to the desired temperature in a flow of nitrogen. After the steady state conditions of temperature and nitrogen flow rate were attained (about 3 to 4 hours), shale oil was metered through the sage pump at a fixed rate (-0.75 ml/min.). During experiments in which steam was used, water was simultaneously injected into the carrier gas and heated in a separate preheater. The steam to nitrogen ratio (vol/vol) was 0.3. The residence time was varied by varying the flow rates of carrier gas. The effects of residence time and temperature were assessed by studying the reaction at temperatures between 425 and 626°C and residence time ranging from 2 to 10 sec. Duration of each run (with shale oil flow) was about 1-1/2 hours, which was considered to be sufficient for the system to attain equilibrium. The total liquid product mix was collected and weighed for mass balance. Liquid and gases were analyzed by gas chromatography as described earlier. The reactor was weighed before (W_i) and after the reaction. A known amount of methylene chloride was added to the reactor to dissolve the tar-like soluble material formed during the reaction. The reactor was dried in air and reweighed (W_f). The difference between the final weight (W_f) and initial weight (W_i) gave the amount of coke formed. The flow meter at the exit of the apparatus gave the amount of gases evolved during the reaction. The total oil loss was defined as follows

$$\% \text{ Total oil loss} = \left(\frac{\text{amount of oil fed-amount of condensate}}{\text{amount of oil fed}}\right) \times 100$$

A total material recovery calculated from amount of condensate, gas and coke was between 95 to 98 percent.

As indicated earlier, several researchers have been using ethylene/ethane, alkene/elkane and naphthalene/(C_{11}+ C_{12}) hydro-carbon ratios to determine the extent of degradation. In addition to these ratios, hydrocarbon gas/coke ratio was also monitored in the present study.

RESULTS AND DISCUSSION

Low Temperature Soaking

The results obtained by refluxing the shale oil at a constant temperature are presented in Table 1. No noticeable oil loss occurs until a temperature of 300°C is reached. Gas evolution occurred at temperatures higher than 300°C, which indicates the commencement of oil degradation at these elevated temperatures. The amount of gas collected was, however, quite small (∿3 percent) at 400°C. Table 2 gives the analysis of gas samples collected at 400°C.

Successive Distillation

During successive distillation and condensation, a considerable amount of oil is converted into coke and hydrocarbon gases. Overall oil losses and those due to coking and gas formation during successive distillation of shale oil (with and without addition of carrier gases) are shown in Figures 1, 2 and 3, respectively.

Figure 1 shows that in the absence of carrier gas the total oil loss at the end of five distillation runs was as high as 35 percent. About 10 to 15 percent of the initial oil is converted to hydrocarbon gas while the rest undergoes slow polymerization leading to solidification (coke formation); gas to coke ratio remained constant around 0.5 to 0.55. No appreciable amount of thermal degradation was observed below 300°C. At temperatures above 400°C, a considerable amount of gas evolved and at 450°C, a solid residue (coke) was obtained. Hydrocarbon gases evolved are richer in ethane than in ethylene (Figure 4). This phenomenon is just the opposite of that observed in vapor phase oil degradation. These findings are in accordance with the reported literature[3,7] and suggest that the mechanism responsible for the oil loss in liquid phase is different from that occurring in vapor phase.

Addition of carrier gas has a beneficial effect on oil yield. When a mixture of steam and nitrogen was bubbled through the shale oil, a total oil loss of 13 percent was observed while the injection of nitrogen alone resulted in a total loss of 20 percent (Figure 1). The use of carbon dioxide resulted in 18 percent oil loss whereas carbon monoxide and hydrogen resulted in 17 and 15 percent oil loss, respectively. Total oil loss decreases by the addition of carrier gas because of the fact that a major portion of the oil is distilled over at much lower temperatures (<300°C) as compared to the run in which no carrier gas is used, thus has less exposure to the high temperature.

Figure 3 shows that about 24 percent coke was formed at the end of five distillation runs when no carrier gas was injected. The use of carrier gas reduced the amount of coke formed. A mixture of steam and nitrogen resulted in 2 to 3 percent coke as compared to 10 percent when nitrogen, carbon dioxide, and carbon monoxide was passed. When hydrogen was used as a carrier gas about 7 percent of the oil was converted to coke (Figure 3). Substantial decrease in the amount of coke formed when steam is added suggests that steam reacts with coke to give gaseous products, according to the coke steam ($C + H_2O \rightarrow CO + H_2O$) and the water gas shift ($CO + H_2 \rightarrow CO_2 + H_2$) reaction. Indeed, the gas analysis shows increased CO_2 and H_2 concentrations thereby substantiating the occurrence of above-mentioned reactions.

Figure 3 shows that the total hydrocarbon gas evolved was 13 percent when no carrier gas was used. About 10 percent hydrocarbon gas evolved when a mixture of steam and nitrogen was used as compared to 6 percent with hydrogen, carbon dioxide and carbon monoxide as a carrier gas.

The use of steam resulted in lowest oil losses because steam reduces the boiling point of most of the compounds present in shale oil and thus the oil is not exposed to high temperatures. Gas analysis for successive distillation (without carrier gas) is presented in Table 2. The ethylene/ethane ratio is plotted as a function of the number of distillation in Figure 4. It decreases from 0.25 to 0.15 and remains practically unchanged beyond this point.

VAPOR PHASE OIL DEGRADATION

Vapor phase thermal degradation of shale oil was studied as a function of two variables, namely, temperature and residence time. A 3^2 factorial design of experiments was used to investigate the main effects and interactions of these two parameters with oil yield as the response. Effect of steam on oil degradation formed another important part of this investigation.

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The dependence of oil degradation on temperature and residence time is pre-sebted in Figure 5, from which it can be seen that the oil loss increases from 18 percent at 425°C to about 55 to 60 percent at 625°C (residence time $\sim$8 to 9 sec.). It should be noticed here that the oil loss curve at 625°C reaches a maximum level at about 6 sec (residence time), beyond which the rate slows down considerably. Thus, at higher temperatures, increase in residence time beyond 6 sec does not seem to have an appreciable effect. At relatively lower temper-atures (below 500°C), about 20 to 25 percent oil loss is observed, which indi-cates that even at these temperatures, a significant amount of oil undergoes degradation.

The conditions under which the cracking was carried out represent those existing inside the large blocks in an in-situ retort. The present results demonstrate that the oil generated in the interior of these large blocks will suffer extensive degradation ($\sim$50 percent) as it migrates to the hot block surface.

The influence of the two factors, residence time (x_1) and temperature (x_2) was determined using a 3^2 factorial design of experiments. The three levels of each factor will be designated by -1, 0, and 1, while the units of the design will be denoted by

$$x_1 = \frac{time - 5}{3} \quad and \quad x_2 = \frac{temp - 525}{100}$$

The oil losses (y) were measured at temperatures of 425, 525 and 625°C, and residence times of 2, 5 and 8 sec. It was assumed that a second-degree equation of the type

$$y = a_0 + a_1x_1 + a_2x_2 + a_{11}x_1^2 + a_{22}x_2^2 + a_{12}x_1x_2 \tag{1}$$

would correlate the oil loss (y) to the temperature and time adequately. The coefficients, evaluated by the method outlined by Davies,[14] were substituted in Equation (1) to give the following equation

$$y = 21.70 + 9.60x_1 + 18.0 \, x_2 - 3.4x_1^2 + 8.26x_2^2 + 2.82 \, x_1x_2 \tag{2}$$

Fig. 6 shows a good agreement between the experimental data and the results calculated from Equation (2) with coefficient of correlation close to 0.99. Thus, one can use Equation (2) to predict the percent oil degradation at 425 to 625°C and 2 to 10 sec residence time.

The data presented in Figure 5 are used to obtain the rate equation for total oil degradation. Kinetics of the oil degradation or cracking can be correlated by a first order rate expression:[10]

$$- \ln (1 - x) = kt \, , \tag{3}$$

where x is the fraction of oil lost, t is the residence time (sec), and k is the first order rate constant (sec^{-1}). Table 3 compares the k values computed from Equation (3) with those reported by Burnham and Taylor[10] and reveals very clearly the two regions of interest, 400 to 500°C, and the high temperature region above 500°C. The k value obtained at 475°C in the present study is 2 to 2.5 times higher than the value reported by them at 506°C, which suggests that the oil yields show strong sensitivity to degradation even at lower temperatures. At higher temperatures, the present results are in fairly good agreement with their data.[10]

Activation energy of 17.3 kcal/mole was obtained from the Arrhenius plot. The activation of 37.1 kcal/mole reported by Burnham and Taylor[10] for thermal cracking of shale oil over burnt shale at 500°C is much higher than that found in the present study. The low activation energy observed in this investigation suggests certain catalytic or auto-catalytic effects exhibited by certain compounds (mineral matter) present in shale or those evolved during the cracking reaction (for example, H_2S).

Figure 7 gives the production of methane as a function of time and temperature. Increase in temperature from 425 to 625°C increases the weight percent of methane by a factor of 6. This data was used to obtain the specific rate constants and activation energy for methane production. In this case also a low value of activation energy (13 kcal/mole) was obtained which supports our supposition that certain autocatalytic effects are taking part in shale oil cracking.

The effect of steam was investigated at various temperatures and residence time. It was not surprising to note that the addition of steam decreased the coke build-up in the reactor. However, it did not seem to have any beneficial effect in reducing the overall oil loss. Hydrocarbon gas/coke, ethylene/ethane and naphthalene/(C_{11}+ C_{12}) hydrocarbons ratios were monitored during the course of cracking reaction. The increase in these ratios clearly shows that the cracking reaction dominates at high temperatures and that the chemical reactions taking place in vapor phase degradation are different from those in liquid phase degradation.

The ratio of hydrocarbon gases to coke formed during the reaction is plotted as a function of temperature in Figure 8 at two residence times (3 and 8 sec). Both the curves exhibit maximum at 525°C beyond which a plateau is observed. Increase in this ratio with temperature suggests that the cracking is more prevalent than coking at higher temperatures.

The ethylene/ethane ratio is plotted as a function of temperature (residence time ~5 sec) and oil loss in Fig. 9. It increases with increase in temperature and oil loss. An interesting phenomenon is that at low temperatures (below 500°C) the ethylene/ethane ratio decreases slightly with an increase in residence time (at a fixed temperature) while at higher temperatures the ratio remains practically constant (independent of the residence time.

It is worth mentioning here that the ethylene/ethane ratio is also a function of whether the oil degradation has taken place in vapor phase or liquid phase. The ratio increases if the oil is subjected to vapor phase degradation, while it decreases when the oil suffers degradation in liquid phase. These results also suggest the mechanism operative in vapor phase is different from that in liquid phase.

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The naphthalene/C_{11} + C_{12}) hydrocarbon ratio was monitored during the shale oil cracking. The following expression was developed to correlate the overall oil loss with this ratio:

$$\% \text{ oil loss} = -0.0185 + 0.129\ R + 1.134\ R^2\ ,$$

where R is naphathalene/(C_{11} + C_{12}) hydrocarbons ratio and (C_{11} + C_{12}) is the sum of undecane, 1-undecene, dodecane and 1-dodecene.

Figure 10 gives the chromatograms of two shale oil samples, one of which was subjected to successive distillation while the other one underwent vapor phase thermal degradation at 625°C. A distinctive feature that needs further consideration is the alkene/alkane ratio. The chromatograms exhibit the characteristic homologous hydrocarbon series ranging from C_{10} through C_{20} with the first peak of each doublet corresponding to the 1-alkene. The sample treated in liquid phase seems to be richer in alkane than in alkene (the ratio alkene/alkane < 1) while that treated at 625°C in vapor phase has an alkene/ alkane ratio for (C_{11} .C_{12},...) greater than unity. These results agree fairly well with the findings of Burnham, et al[15,16] Campbell, et al[2,3,4] and Uden, et al.[8,9]

<div align="center">CONCLUSIONS</div>

The present results lead us to the following conclusions:

1.   The experimental design described in this paper permits a separate study of the principal mechanisms of shale oil degradation under steady state conditions equivalent to retorting conditions.

2.   Low-temperature, long-term soaking below 300°C showed only minor oil losses while successive distillation and condesation under autogenous conditions showed considerable oil losses (~35 percent). During vapor phase thermal crack-ing about 55 percent oil loss occurs over 5 to 6 sec (residence time) at 625°C.

3.   The steam suppressed coke formation and oil degradation during successive distillations (liquid phase) but it did not seem to reduce the over-all oil loss during vapor phase thermal cracking.

4.   The injection of carrier gas during distillation helped in reducing total oil loss.

5.   The ethylene/ethane and alkene/alkane ratios decreased when oil suffered degradation in liquid phase (coking) while all the ratios used as indices of oil degradation increased with increase in oil loss due to cracking (vapor phase).

6.   Minimizing the gas phase residence time in large retorts should improve oil yields.

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Table 1

Low Temperature Soaking Results Under Refluxing Conditions

Temperature (°C)	Coke (%Wt)	Liquid Condensate (%Wt)	Gases (%Wt)	Liquid in Still (%Wt)
150	nil	--	--	99.0
200	nil	1.0	0.1	98.5
250	nil	1.5	0.4	98.0
300	nil	17.0	0.5	81.0
350	nil	30.0	1.0	68.1
400	nil	47.1	3.0	47.6

Table 2

Analysis of Gases
(temperature of reaction = 400°C)

Gas Composition (%Wt)

	I*	II**
Hydrogen	<1	<1
Methane	44.3	41.4
Ethylene	2.2	2.8
Ethane	11.1	17.7
Propylene	3.2	3.7
Propane	15.0	18.3
Butenes and Butanes	16.9	15.5
Pentenes and Pentanes	6.1	5.1
$CO + CO_2$	<1	<1

*I - Low temperature coking.
**II - Successive distillation and condensation.

Table 3

Specific Reaction Rate Constants at Various Temperatures

Temperature °C	Present Work sec^{-1}	Literature Values[10] sec^{-1}
475	0.026	--
506	--	0.01
525	0.046	--
558	--	0.04
575	0.086	--
585	--	0.10
610	--	~0.15
625	0.178	--

Figure 1. Percent hydrocarbon gases produced versus number of distillations. (Same symbols as in Figure 1 are used.)
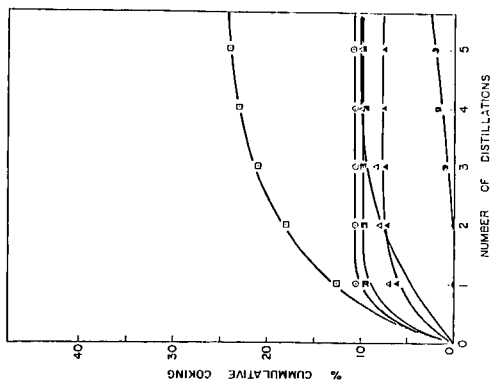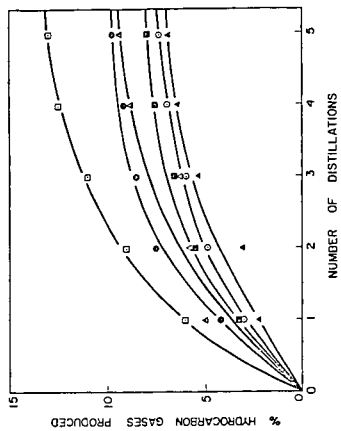
Figure 2. Percent cumulative oil loss versus number of distillations. (Same symbols as in Figure 1 are used.)

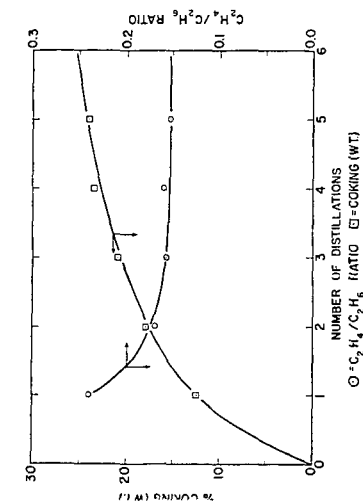Figure 1. Percent total overall loss versus number of distillations. (□) no gas addition; (△) adding nitrogen; (○) adding steam and nitrogen; (▲) adding hydrogen; (●) adding carbon monoxide; (⊡) adding carbon dioxide.
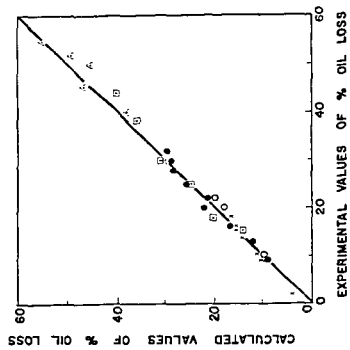
Figure 6. Experimental and predicted values (Eqn. 2) of % oil loss, at various temperatures. Solid lines represent the predicted values while experimental values are shown by the same symbols used in Figure 5.
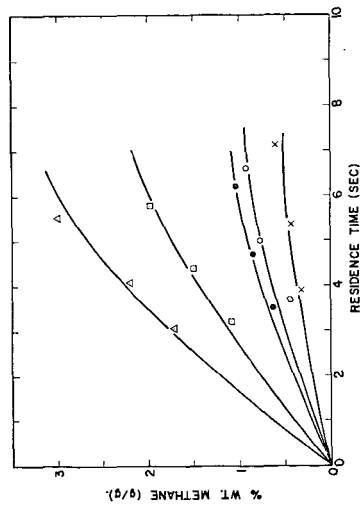

Figure 5. Dependence of shale oil degradation (wt%) on residence time at various temperature. (X) 425°C, (O) 475°C, (□) 525°C, (●) 575°C, (△) 625°C.

Figure 4. Ethylene/ethane ratio and percent coke as a function of number of distillations when no carrier gas was passed.

O =C_2H_4/C_2H_6 RATIO   □=COKING (WT)

Figure 8. Hydrocarbon gas/coke ratio versus temperature at residence time. 3 sec (⊙) and 8 sec (⊡).

Figure 7. Percent methane (q/q oil) produced as a function of residence time and temperature. (Same symbols as in Figure 5).
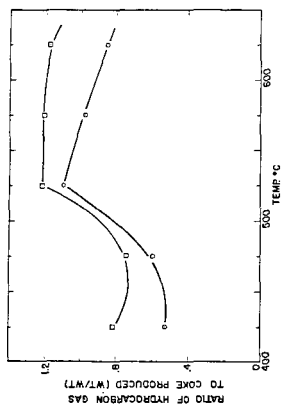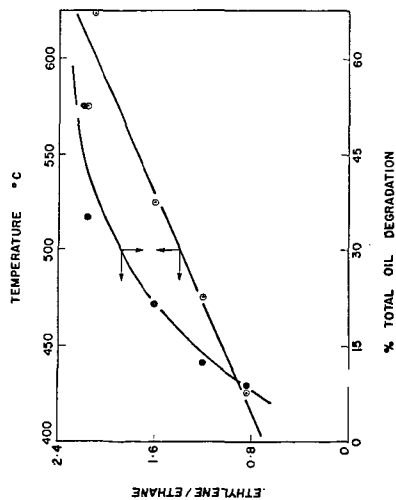
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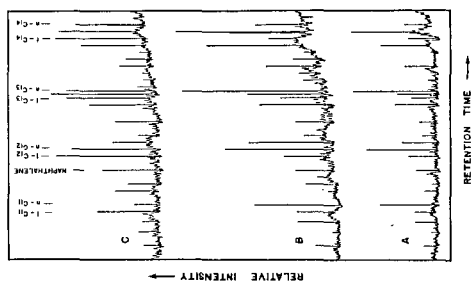Figure 9. Ethylene/Ethane ratio against the reaction temperature at residence time of 5 sec.

Figure 10. Chromatograms of various samples: a. raw shale oil; b. shale oil subjected to liquid phase degradation (below 450°C); c. shale oil subjected to vapor phase degradation (625°C).